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Preconcentration method for trace metals in natural waters using 4-morpholine dithiocarbamate

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Abstract: The optimum conditions were found for the preconcentration of trace metals in natural waters and model samples with standard metals concentrations by using 4-morpholine dithiocarbamate. The formed complexes were extracted with chloroform. Different methods for recovering the metals from the organic solvent were studied and compared before AAS metal analysis. The developed preconcentration method was successfully applied to the determination of trace metals concentrations in water samples from the "Barje" lake (Leskovac, Yugoslavia).

Keywords: preconcentration, chelating extraction, water analysis.

INTRODUCTION

Heavy metals contamination is a common problem encountered in different parts of the environment. Once released into the ecosystems, most heavy metals are strongly retained and their adverse effects can last for a long time. The problem is exacerbated in the chemical analysis by low concentrations of metals, so many times they are under the detectable value. Chelating extractions of heavy metals from investigated water samples is a relatively new treatment method. In the literature, a large number of chelators have been studied. Lead, copper, cadmium, zinc, nickel, cobalt, manganese nad iron can be extracted from the water using a mixture of sodium diethyldithiocarbamate,[1–3] ammoniumtetramethylenedithiocarbamate,[4] hexamethylene-bisdithiocarbamate,[5] ammoniumpyrrolidinedithiocarbamate.[6–10] quinolin-8-ol,[11] potassium dibutylphosphorodithionate,[12] sodium debenzyldithiocarbamate,[13] methanolic 2 % hexahydroazepinium-hexahydroazepine-1-carbodithionate,[14] and many others. The complexes were extracted using various organic solvents: $CHCl_3$,[1,6] isobutyl-methyl ketone,[5,7–9] CCl_4,[2,3,11,12] a mixture of $CHCl_3$ and methanol (1:1),[13] xylene,[14] di-isobutyl ketone,[10] *etc*. The trace metals in the organic phase can be determined directly by

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AAS,[7,9,10,12] or the organic phase can be evaporated to dryness and the residue repeatedly digested by heating with conc. HNO_3, dilution and analysis by AAS.[2,6,11] The trace metals can be transferred back into aqueous solutions by treatment of the organic extract with a mixture of HNO_3 and H_2O_2 and the metals determined by AAS,[8] also addition metals like Hg^{2+} and Pd^{2+} which make more stable complexes than the trace metals can be used for trace metals recovery.[4]

Preconcentrations can be performed by passing a large volume of the water sample through a column packed with any immobilized phase. The adsorbed metals are then eluted by a suitable acid. Thus, Horvath *et al.*[15] determined the trace metals in a rainwater sample after preconcentration on an iminodiacetic acid ethylcellulose microcolumn in the NH_4^+ form. The rainwater was adjusted to pH 5–6 and than passed through the microcolumn at 2.5 ml/min. The retained metal ions were eluted with 2 M HCl and Cd, Co, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn were determined by ICP AES. Chang *et al.*[16] preconcentrated trace metals on poly(acrylonitrile) fibre packed in a glass tube. Sample solutions were adjusted to pH 6 with dilute NH_3 before being passed through the column at 6 ml/min. The adsorbed cations were desorbed with 3 M HCl/0.6 M H_2SO_4/0.5 M HNO_3 and analyzed by ICP AES. After regeneration, the fiber column could be reused ten times. Esser *et al.*[17] and Lan, Yan[18] preconcentrated trace metals in waters using silica-immobilized 8-hydroxyquinoline. Kobayashi *et al.*[19] preconcentrated trace metals by passing samples through a column packed with 3-chloropyridazine-6-carboxylic acid hydrazide, which was coupled to amino-aryl-controlled pore glass beads. Wang *et al.*[20] preconcentrated water by passing it through a column packed with activated carbon and quinolin-8-ol, and elution with 4 M HNO_3. The same investigators also used a column packed with cotton, which had been macerated for 24 h with 4 M HCl and washed to pH 7 with H_2O. The adsorbed ions were eluted with 4 ml of 4 M HCl before analysis by AAS.

Extractions can be combined with HPLC determinations. Therefore Shofstahl and Hardy[21] mixed water samples with sodiumdibenzyldithiocarbamate. The mixture was shaken with $CHCl_3$ and the organic phase was reserved for a later stage. The aqueous phase was then made alkaline with phosphate buffer and extracted with isobutyl-methyl ketone. Both extracts were evaporated to dryness and the residues were dissolved in $CHCl_3$. The extracts were analyzed on a Alltech C18 column. The mobile phase consisted of methanol – acetonitrile – THF – acetate buffer of pH 5 (64:12:5:19). Detection was at 254 nm. The method was applicable for the determination of Cd, Cr, Cu, Hg, Mn, Pb, Sb, Se, Tl and Zn; the detection limits were 0.1 to 1.8 ppb. The results were compared with those obtained by AAS.

A comparative study of preconcentration methods was also made by Vernon and Wani[6] who compared evaporation, complexation with ammonium pyrrolidine dithiocarbamate and passing through a Dowex 50 cationic exchange resin column. They mixed river water with the chelating agent ammonium pyrrolidine dithiocarbamate and extracted twice with $CHCl_3$. The $CHCl_3$ was evaporated to dryness and the residue repeatedly digested by heating with conc. HNO_3. A further portion of river water was adjusted to pH 5.2, passed through a Dowex 50 cationic exchange resin column and the metals were

eluted by 2 M HNO_3, before AAS. The results of the determination of Cd, Cu, Pb and Zn by the three concentration methods and by direct electrothermal AAS were compared. The results for the preconcentration methods agreed well with recoveries from a standard solution of 91 – 101 %.

The goal of this work was to assess the potential of extraction and recovery of heavy metals using 4-morpholine dithiocarbamate as chelator. The investigated preconcentrated methods are compared with evaporation as a reference procedure.

EXPERIMENTAL

All chemicals used were of analytical-reagent grade, produced by Merck. Distilled water was prepared by distilled deionized water after the addition of potassium permanganate. Nitric acid used in the experiments was suprapure grade. Stock solutions of the heavy metals were prepared by accurate weighing. These solutions were used for the preparation of standard solutions of desired compositions.

Procedure

Appropriate volumes (5.00 ml) of 0.01 M stock solutions were diluted up to 500 ml to obtain standard solutions of 10^{-5} M or 10^{-6} M concentrations. 100 ml samples of these solutions were taken. The solutions were heated at 80 ºC, mixed with 10 ml of 1 % 4-morpholine dithiocarbamate and heating was continued for one hour. The solutions were cooled and transferred into a separation funnel. The formed complexes were extracted three times with 10 ml $CHCl_3$. Recovery of the heavy metal complexes was performed in three different ways:

– First, the combined $CHCl_3$ extracts were evaporated to dryness and the residue repeatedly digested by heating with 2 ml of conc. HNO_3 and diluted up to volume in 25 ml volumetric flasks.

– Second, the heavy metals complexes were extracted from the $CHCl_3$ solutions twice with 10 ml of 4 M HNO_3 solutions and diluted up to volume in 25 ml volumetric flasks.

– Third, the combined $CHCl_3$ extracts were mixed twice with 10 ml of 4 M $HgCl_2$. Then the combined aqueous solutions were diluted up to volume in 25 ml volumetric flasks.

The investigated extracts were analyzed using a flame atomic absorption spectrophotometer "SpectraAA-20+Varian". The metal standards for calibration of the atomic absorption spectrometer were made not more than one hour before use from 10 mg/L stock solutions.

RESULTS AND DISCUSSION

Simple evaporation of water samples, although a very accurate method for preconcentration, takes a very long time. For instance, to evaporate a one liter sample without boiling can take more than a few days. Chelating extractions of heavy metals are an easier and faster procedure. Our investigations have shown that chelating extractions by 4-morpholine dithiocarbamate can be successfully applied (Table I and Table II). The formed complexes can be easily extracted with a small volume of $CHCl_3$, because they dissolve better in the organic solvent than in the water solution. Direct trace metals analysis from the organic solvents by atomic absorption spectrometry can cause problems so our attention was focused on solving quantitatively the extraction of the trace metals from the organic solvent into the small volume of an aqueous layer. As describe above, three different methods were used. Evaporating the organic solvents and dissolving the residues in small volumes of an acidic solution was found to be the most accuarate but also the slowest procedure. For all the tested heavy metals, a recovery of slightly less than 100 % was found.

These methods have almost the same recovery as the simple water evaporation procedure.

TABLE I. Recovery after the preconcentration procedure for standard solutions containing 10^{-5} M of trace metal

Metals	Taken	Evaporated		Mean recovery ± standard deviation of three replicates					
				Extrated with $CHCl_3$; evaporated and dissolved in HNO_3		Extracted with $CHCl_3$; re-exatracted with HNO_3		Extracted with $CHCl_3$; re-extracted with Hg^{2+}	
	µg	µg	%	µg	%	µg	%	µg	%
Fe	559.14	547.4	97.9	550.6	98.5	532.0	95.2	516.5	92.4
		±14.3	±2.6	±8.8	±1.6	±4.3	±1.6	±3.3	±0.6
Mn	550.70	536.2	97.4	535.4	97.2	530.4	96.3	513.6	93.3
		±8.7	±1.6	±6.7	±1.2	±6.5	±1.2	±3.0	±0.5
Ni	593.00	587.2	99.0	575.5	97.0	564.8	95.2	549.6	92.7
		±8.7	±1.7	±9.6	±1.6	±3.0	±0.5	±2.9	±0.5
Co	587.44	572.0	97.4	570.8	97.2	561.1	95.5	540.0	91.9
		±9.3	±1.6	±5.2	±0.9	±2.0	±0.3	±1.4	±0.2
Cu	633.93	622.6	98.2	619.5	97.7	607.7	95.9	579.7	91.4
		±11.9	±1.9	±10.5	±1.6	±3.6	±0.6	±1.6	±0.2
Zn	654.32	645.7	98.7	636.8	97.3	626.2	95.7	601.0	91.9
		±6.7	±1.0	±5.4	±0.8	±1.8	±0.3	±0.4	±0.1
Pb	2072.00	2023.9	97.7	2015.8	97.3	1980.4	95.6	1900.3	91.7
		±25.4	±1.2	±18.7	±0.9	±35.2	±1.7	±6.6	±0.3
Cd	3373.65	3317.4	98.3	3295.8	97.7	3205.6	95.0	3104.0	92.0
		±26.1	±0.8	±37.0	±1.1	±19.3	±0.6	±1.3	±0.0

Mean ± standard deviation of three replicates

Re-extraction by a small volume of 4 M HNO_3 has the advantage because it is a faster method than the methods described above, but the recovery was slightly less. Recoveries of more than 95 % were found for all the studied heavy metals.

Re-extraction of the trace metal complexes by 4 M $HgCl_2$ solutions from the $CHCl_3$ solvents gave recoveries ranging from 90 to 93 %. The reason for this can be found in the relations between the stability constants for mercury and the heavy metals.

The developed preconcentration methods using 4-morpholine dithiocarbamate as a chelating agent was successfully applied to the determinations of the concentrations of trace metals in water samples from the "Barje" lake sampled on September 25th, 2000. The formed complexes were extracted three times with $CHCl_3$ solvent, and the complexes were re-extracted twice with 4 M HNO_3. The extracts were diluted (25 ml) and analyzed by AAS. Simple evaporation of the water samples was used as the reference method. The results are compared in Table III.

TABLE II. Recovery after the preconcentration procedure for standard solutions containing 10^{-6} M of trace metal standard solutions

Metals	Taken	Evaporated		Mean recovery ± standard deviation of three replicates					
				Extrated with $CHCl_3$; evaporated and dissolved in HNO_3		Extracted with $CHCl_3$; re-exatracted with HNO_3		Extracted with $CHCl_3$; re-extracted with Hg^{2+}	
	µg	µg	%	µg	%	µg	%	µg	%
Fe	55.9	55.3	98.9	54.6	97.6	54.3	97.2	51.3	91.7
		±0.7	±1.3	±1.2	±2.1	±0.8	±1.4	±1.3	±2.3
Mn	55.1	54.2	98.5	53.4	96.9	53.6	97.3	50.8	92.3
		±1.7	±3.0	±0.7	±1.3	±0.8	±1.4	±0.7	±1.2
Ni	59.3	57.7	97.3	58.0	97.9	57.6	97.1	54.7	92.2
		±1.9	±3.3	±1.0	±1.6	±0.9	±1.6	±1.5	±2.5
Co	58.7	56.9	96.8	57.0	97.0	57.2	97.4	53.2	90.6
		±1.1	±1.9	±1.1	±1.8	±1.2	±2.0	±1.7	±2.8
Cu	63.4	61.6	97.1	62.0	97.7	60.9	96.1	57.2	90.2
		±1.5	±2.4	±1.6	±2.6	±1.7	±2.7	±1.1	±1.7
Zn	65.4	64.3	98.3	63.6	97.1	63.5	97.0	59.7	91.2
		±1.0	±1.5	±1.1	±1.6	±0.8	±1.2	±0.9	±1.4
Pb	207.0	201.9	97.4	200.3	96.7	199.7	96.4	190.6	92.0
		±2.4	±1.1	±2.8	±1.4	±2.5	±1.2	±1.0	±0.5
Cd	337.4	328.5	97.4	326.9	96.9	326.4	96.7	313.5	92.9
		±3.9	±1.2	±1.9	±0.6	±2.0	±0.6	±4.2	±1.3

Mean ± standard deviation of three replicates

TABLE III. Results for the trace metal concentrations in water from three locations of the "Barje" lake. (Evap. = Preconcentration by evaporating 1 L of the water sample; Extr. = Preconcentation of 1 L of the water sample by chelating extraction with 4-morpholine dithiocarbamate)

Metals		Dam of the accumulation lake µg/L			Midle of the accumulation lake µg/L			Main tributary (Veternica) µg/L
Depth bellow interface		0.5 m	15 m	30 m	0.5 m	15 m	30 m	0.5 m
Fe	Evap.	136±7	331±16	546±17	114±9	275±18	422±15	126±8
	Extr.	128±6	325±14	529±12	105±10	260±8	412±9	122±4
Mn	Evap.	22±4	63±6	88±6	15±1	41±2	65±3	21±2
	Extr.	20±4	57±5	78±4	13±2	35±4	61±4	17±2

TABLE III. Continued

Metals		Dam of the accumulation lake µg/L			Midle of the accumulation lake µg/L			Main tributary (Veternica) µg/L
Depth bellow interface		0.5 m	15 m	30 m	0.5 m	15 m	30 m	0.5 m
Ni	Evap.	14±3	24±4	27±4	14±2	23±2	28±2	14±2
	Extr.	11±2	21±3	20±5	11±2	20±2	23±3	12±2
Cu	Evap.	22±3	28±3	29±4	22±3	27±2	28±4	19±2
	Extr.	18±3	25±2	26±2	18±3	23±2	25±2	15±1
Zn	Evap.	30±2	34±2	41±3	27±2	28±3	39±2	19±2
	Extr.	25±3	30±3	35±3	25±2	25±2	34±3	15±3
Pb	Evap.	16±1	19±2	26±2	13±2	14±2	26±2	13±2
	Extr.	12±1	17±3	22±1	11±1	12±2	23±3	11±2
Cd	Evap.	3±1	4±1	4±1	2±1	3±1	3±0	1±0
	Extr.	2±1	3±1	3±1	2±0	3±1	3±1	1±0

Mean ± standard deviation of three replicates

CONCLUSION

Chelating extraction preconcentration using 4-morpholine dithiocarbamate as the chelator was successfully applied. The studied methods were compared with simple evaporation of the water samples as the reference procedure. The formed complexes were extracted many times with small volumes of $CHCl_3$. Recovery of the heavy metal complexes from the organic solvent was conducted in three different ways: by evaporating the organic solvent and dissolving the residue in a small volume of dilute nitric acid; by double extracting with a small volume of dilute nitric acid and by mixing with Hg^{2+} solutions. Comparison of the results showed that the recovery was more than 95 % when the first two methods were used but that it was only between 90 to 93 % when the third procedure was applied.

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ИЗВОД

ПРЕТКОНЦЕНТРАЦИЈА МИКРОЕЛЕМЕНАТА ИЗ ВОДЕ КОРИСТЕЋИ 4- МОРФОЛИН ДИТИОКАРБАМАТ

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Нађени су оптимални услови за претконцентрацију микроелемената из воде користећи 4 морфолин дитиокарбамат као комплексирајући агенс. Награђени комплекси су екстрахо-

вани хлороформом. Упоређени су различити начини екстракције металних јона из органског растварача пре анализе атомском апсорпционом спектрофотометријом. Развијена метода за претконцентрацију успешно је примењена за анализу узорака воде језера Барје (Лесковац, Југославија).

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